## (19) World Intellectual Property Organization International Bureau





## (43) International Publication Date 12 September 2002 (12.09.2002)

## **PCT**

# (10) International Publication Number WO 02/071520 A1

(51) International Patent Classification<sup>7</sup>: H01M 8/00, 8/12, 4/00

(21) International Application Number: PCT/US02/04161

(22) International Filing Date: 13 February 2002 (13.02.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

09/798,314 2 March 2001 (02.03.2001) US

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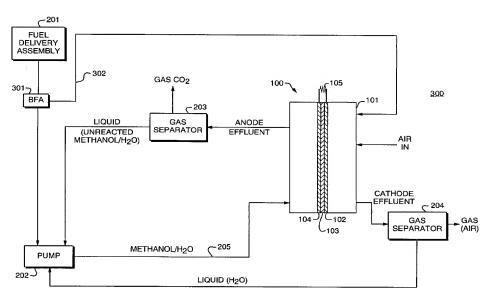
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

[Continued on next page]

(54) Title: COLD START AND TEMPERATURE CONTROL METHOD AND APPARATUS FOR FUEL CELL SYSTEM



(57) Abstract: A fuel cell (100) which provides improved performance during a cold start. Several embodiments are provided to enable the controlled introduction of fuel into the cathode (202) of the fuel cell (100) such that oxidation occurs, heat is released and the temperature of the fuel cell (100) is raised. Such fuel may be introduced into the cathode (202) directly or may be introduced into the anode (204) and allowed to crossover an electrolytic membrane. Alternatively, the fuel may be directed through a special conduit (205) which allows oxidation of some of the fuel as it flows through.

02/071520 A1

## WO 02/071520 A1



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- 1 -

# COLD START AND TEMPERATURE CONTROL METHOD AND APPARATUS FOR FUEL CELL SYSTEM

## BACKGROUND OF THE INVENTION

## Field of the Invention

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The present invention relates generally to the field of fuel cells and, more specifically, to a fuel cell system in which the temperature within the cell may be raised and controlled to improve performance in cold environments.

## **Background Information**

Fuel cells are devices in which an electrochemical reaction is used to generate electricity. A variety of materials may be suitable for use as a fuel, depending upon the materials chosen for the components of the cell. Organic materials, such as methanol or formaldehyde, are attractive choices for fuels due to their high specific energies.

Fuel cell systems may be divided into "reformer based" (*i.e.*, those in which the fuel is processed in some fashion before it is introduced into the cell) or "direct oxidation" in which the fuel is fed directly into the cell without internal processing. Most currently available fuel cells are of the reformer-based type, and their fuel processing requirement limits their application to relatively large applications relative to direct oxidation systems.

An example of a direct oxidation system is the direct methanol fuel cell system or DMFC. In a DMFC, the electrochemical reaction at the anode is a conversion of methanol and water to CO<sub>2</sub>, H<sup>+</sup> and e<sup>-</sup>. More specifically, a carbonaceous fuel (typically methanol in an aqueous solution) is applied to a protonically-conductive, electronically non-conductive membrane in the presence of a catalyst to enable direct anodic oxidation of the carbonaceous fuel at the anode. Upon contact with the catalyst, hydrogen atoms from the fuel are separated from the other components of the fuel molecule. Upon closing of a circuit connecting the anode to the cathode through an ex-

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ternal load the protons and electrons from the hydrogen are separated, the resulting protons pass through the membrane electrolyte, and the electrons travel through an external load. The protons and electrons combine on the cathode, with oxygen supplied to the cathode, generating water at the cathode. The carbon component of the fuel is converted into CO<sub>2</sub> at the anode, thus generating additional protons and electrons.

Present membrane electrolytes are permeable to methanol and water. Consequently, methanol may pass through the membrane electrolyte to the cathode side without generating electricity. This phenomenon, commonly referred to as "methanol crossover," reduces the efficiency of the DFMC, and generates heat as a result of the oxidation of the "crossed-over" methanol at the cathode side of the cell. Presently, methanol crossover is reduced by diluting the methanol with water, and using a methanol solution of approximately 3% methanol as fuel for a DMFC.

During optimal steady state operation, DMFCs operate at temperatures that are generally higher than ambient air temperatures, with most operating between 30° and 80°C, depending on the application for which the DMFC is providing power. The performance of the DMFC (and therefore the DMFC power system) is related to the temperature of the DMFC. Thus, when a DMFC has been inactive for an extended period of time or is required to operate in a cold ambient environment, the DMFC will typically not perform optimally until the cell is warmed up by heat that is generated during operation. This is particularly problematic in applications such as consumer electronic devices because such devices may be used in cold environments or are "off" for substantial time periods, during which time the DMFC may cool below an optimal operating temperature. It is therefore desirable to develop a system that allows a DMFC to ramp up to full operating temperature quickly to allow for generation of desired electricity as quickly as possible.

## SUMMARY OF THE INVENTION

The present invention provides an apparatus and method for increasing the temperature of a fuel cell, such as a DMFC, and maintaining it at an optimal level by directing fuel to the cathode in order to cause heat-producing oxidation. By increasing the temperature in the fuel cell, "cold start" performance of the fuel cell is improved.

In a preferred embodiment, fuel is supplied directly to the cathode side of the fuel cell through a bypass fuel assembly, rapidly generating heat within the cell. The bypass fuel assembly includes a temperature sensor, a controller and a bypass valve. The sensor detects the temperature within the cell and sends a signal indicative of the temperature to the controller. In response to the signal from the temperature sensor, the controller determines whether to direct fuel to the cathode via the bypass valve in order to raise the cell's temperature. Alternatively, electrical or other characteristics of the fuel cell can be used to direct flow of methanol to the cathode, and eliminate the need for a temperature sensor in the fuel cell.

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In accordance with a first alternative embodiment of the invention, additional fuel beyond that needed to operate the fuel cell is applied to the anode. The increased concentration of fuel in the anode accelerates crossover of fuel through the membrane electrolyte, thereby increasing the amount of fuel present in the cathode and, in turn, the amount of heat generated by oxidation.

In accordance with a second alternative embodiment of the invention, a conduit is provided between a fuel source and the anode or cathode of the DMFC. The sidewall of the conduit includes an assembly which may admit air from outside the conduit and a catalyst over which the fuel passes. As the fuel flows through the conduit, the catalyst causes oxidation of some of the fuel, thus generating heat which is carried into the anode or cathode or both to raise the temperature of the DMFC and the DMFC power system. By expanding the conduit into a series of branches, at least some of which include the catalytic assembly, and arranging a number of valves among the branches, the amount of heat generated may be more precisely controlled. Alternatively, a single branching conduit can be equipped with a metering valve that controls the flow through the conduit and thereby regulates the temperature of the DMFC.

In accordance with another aspect of the invention, the flow of fuel which is being used to raise the temperature of the DMFC is controlled with a control valve that is either electrically or thermally actuated. In the thermally actuated version, a valve may be constructed of two materials having different coefficients of expansion. When the temperature is relatively cold, the valve is open and allows fuel to flow to the DMFC, which eventually raises the temperature. As the temperature rises sufficiently

WO 02/071520

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high, the valve closes and cuts off the flow of fuel. As a result, the DMFC's temperature is well regulated without the need for a temperature sensor, controller or bypass valve.

## BRIEF DESCRIPTION OF THE DRAWINGS

- The invention description below refers to the accompanying drawings, of which:
  - Fig. 1 is a block diagram of a direct methanol fuel cell known in the prior art;
- Fig. 2 is a block diagram of a direct methanol fuel cell power system known in the prior art;
- Fig. 3 is a block diagram of a direct methanol fuel cell power system constructed in accordance with a preferred embodiment of the present invention;
- Fig. 4 is a block diagram of a direct methanol fuel cell power system constructed in accordance with a first alternative embodiment of the present invention;
  - Fig. 5 is a block diagram of the bypass fuel assembly of Figs. 3 and 4;
- Fig. 6 is a block diagram of a conduit used in a second alternative embodiment of the present invention;
- Fig. 7A is a block diagram of a conduit branching arrangement for use in the embodiment of Fig. 6 in the present invention;
- Fig. 7B is a block diagram of a closed end conduit which incorporates the oxidation pack of Fig. 6;
- Figs. 8A and 8B are cross-sectional schematic views of a valve or conduit of a third alternative embodiment of the present invention; and
- Fig. 9 is a flow chart of a method for controlling temperature in a direct methanol fuel cell.

# DETAILED DESCRIPTION OF AN ILLUSTRATIVE EMBODIMENT

Figure 1 shows a schematic diagram of a direct methanol fuel cell (DMFC) 100 known in the prior art in which a housing 101 encloses a cathode 102, a membrane electrolyte 103, and an anode 104. A load 105 is connected across cathode 102 and an-

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ode 104. Methanol or a methanol/water solution are introduced into the anode 104 side of housing 101 while oxygen is introduced into the cathode 102 side of the housing 101. The source of the oxygen is preferably ambient air, but other sources could be used. As a result of the reactions at the anode 104 and cathode 102, electrons flow through wires from anode 104 through load 105 to cathode 102, while hydrogen ions flow from anode 104 through membrane 103 to cathode 102. So long as the reactions continue and the circuit is closed, a current is maintained through load 105.

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DMFC 100 may be constructed from a variety of commercially available materials using proton conducting membranes (such as Nafion®, available from E.I. DuPont de Nemours and Company) and catalysts such as a Platinum/Ruthenium mixture (available from Johnson Matthey, PLC and other specialty companies) or acid-filled porous separators. The remaining components of DMFC 100 can be constructed using existing fabrication techniques and readily available materials.

Referring to Fig. 2, a direct methanol fuel cell (DMFC) power system 200 with which the temperature control system of the present invention may be used, is illustrated. Fuel from a fuel delivery assembly 201 is supplied directly to a pump 202 or, alternatively, may be supplied to a reservoir (not shown) positioned upstream from the pump. Pump 202 is supplied with or draws liquid from anode effluent, through a gas separator 203, and from cathode effluent through a second gas separator 204, pumping the fuel solution to anode of DMFC 100 via conduit 205. Gas separators 203 and 204 may be based on a CO2 permeable/water impermeable membrane, or a variety of other techniques known in the art. The present invention is not dependent upon the presence of gas separators and may be used with fuel cell systems which do not include such separators.

Gas separator 203 receives effluent from anode 104 and separates it into liquid (*i.e.*, unreacted methanol or methanol and water) and carbon dioxide gas which is vented to the external environment. The liquid component is returned to pump 202 for recirculation to DMFC 100. The gas component may, alternatively, be returned to pump 202 and used to drive the pump in accordance with the teachings of commonlyowned U.S. patent application Serial No. 09/717,754. Pump 202 may be designed so as to control the proportions of flow of each of the water, neat methanol, and fuel solution

- 6 -

input streams. Referring to Fig. 3, DMFC power system 200 of Fig. 2 is illustrated with the addition of a bypass fuel assembly (BFA) 301. Bypass fuel assembly 301 operates to supply fuel to the cathode 102 of DMFC 100 through a conduit 302. Such fuel reacts with oxygen (from ambient air or other source) normally present in cathode 102, oxidizes and generates heat which raises the temperature of DMFC 100. It is preferred that bypass fuel assembly 301 supply "neat" fuel that has not been circulated through the system as neat fuel is more highly concentrated and thus generates heat at a faster rate upon oxidation. If desired, a fuel source other than fuel delivery assembly 201 (not shown) may be used to provide fuel to BFA 301. It should be understood that the fuel delivery system may include an internal fuel tank, an external fuel cartridge or a combination of internal and external sources.

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Fig. 4 shows an alternative embodiment of the present invention in which DMFC power system 300 of Fig. 3 is modified by the omission of conduit 302 and the addition of conduit 401. In this embodiment, conduit 401 supplies fuel from BFA 301 to anode 104 of DMFC 100. Fuel supplied via conduit 401 effectively increases the concentration of fuel at anode 104, thereby increasing methanol crossover through membrane 103. Alternatively, BFA 301 may be used to increase the flow of fuel pump 202, thereby increasing the concentration of fuel in conduit 205 and, in turn, the concentration of fuel at anode 104. The higher fuel concentration results in increased methanol crossover, causing additional methanol to oxidize at cathode 102, thus increasing the temperature of the DMFC 100 and the DMFC power system 200. Such crossover results in increased methanol in the cathode 102 side of DMFC 100 that oxidizes and produces heat. System 400 increases the temperature in DMFC 100 at a slower rate than system 300. It will be understood by those skilled in the art that it may be advantageous to construct a system that combines systems 300 and 400. Such a combined system, if used appropriately, would provide both fast heating, as required to raise the temperature of a DMFC to optimal operating temperatures quickly, as well as effective control of the temperature of the DMFC during continuous operation.

Referring to Fig. 5, a preferred embodiment of bypass fuel assembly 301 is shown in block diagram form. A controller 501 is coupled to a temperature sensor 502 and a valve 503. Temperature sensor 502 senses the temperature in DMFC 100 or

- 7 -

DMFC power system 200 and sends a signal indicative of same to controller 501. Based on the sensed temperature, controller 501 opens or closes valve 503 to direct more or less methanol to DMFC 100, thus raising or lowering the temperature as appropriate.

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Temperature sensor 502 may be implemented using any of a variety of commercially available direct temperature measurement devices, such as a thermocouple. Alternatively, an indirect method of temperature measurement may be used, including, but not limited to measuring the voltage or current produced by DMFC 100. This is possible because it is known that the operating temperature of DMFC 100 is closely related to its power output. Thus, by measuring the voltage at a given current or current at a given voltage produced by DMFC 100, the temperature may be calculated or obtained by reference to a lookup table based on the power/temperature relationship. Other relationships exist that may be used to indirectly measure the temperature of the DMFC, including, for example only, the generation of carbon dioxide and water over given periods of time.

Fig. 6 shows an alternative embodiment of the present invention in which a conduit assembly 600 is used to generate heat to raise the temperature of DMFC power system 200 or 300. The structure of conduit assembly 600 may be used to implement conduit 205 (Fig. 2), conduit 302 (Fig. 3), other conduits within or attached to a DMFC, a separate conduit which is exclusively dedicated to the function of heat generation, or a combination of the foregoing. An oxidation pack 601 is integrated into a conduit wall 604. It should be understood that more than one oxidation pack could be integrated within conduit wall 604. Oxidation pack 601 includes an air permeable membrane 602 and a catalyst/supporting material 603. Catalyst/supporting material 603 is exposed to the interior of conduit assembly 600 such that when neat methanol or aqueous methanol solution passes over it heat-producing oxidation takes place. Air to support the oxidation is made available by a membrane 601 that is gas permeable but impermeable to neat methanol, water, or aqueous methanol solution.

In order to control the amount of heat generated by conduit assembly 600, some arrangement for controlling the flow of methanol through the conduit is needed. Fig. 7A shows one such arrangement in block diagram form. A series of oxidation packs

601a-601f are disposed on a series of conduit branches 701a-701f. Valves 503a-501f provide the ability to shut off particular branches 701 if less heat is needed. For example, if controller 501 (Fig. 5) receives a higher temperature reading from sensor 502 (*i.e.*, less heat is needed), then controller 501 may close valve 503b and cut off oxidation pack 601c Similarly, closing valve 503a effectively cuts off oxidation packs 601a, 601c and 601d as a group. In this fashion, the amount of heat generated may be rapidly or slowly increased or decreased as appropriate. Alternatively, the flow of air over oxidation packs 601, rather than the flow of methanol within the conduit, could be regulated to control the rate of oxidation. Such air regulation could be accomplished through incorporating a series of valves, seals or other devices or assemblies known to those skilled in the art.

Fig. 7B shows a closed end conduit 700 which uses three oxidation packs 601g-601i to form an oxidation plenum 702. A valve 701 controls the flow of fuel into plenum 702. Closed end conduit 700 may be substituted for conduit assemblies 600c-600f in Fig. 7A.

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Referring to Figs. 8A and 8B, an alternative embodiment of the present invention is shown. A valve 803 is constructed of two different materials. A base material 802 preferably has a low thermal expansion coefficient such that temperature changes have little or no effect on its shape or volume. Some examples of such material are silicon or chemically inert plastics. An expansion material 801 preferably has a relatively high thermal expansion coefficient such that an increase in temperature causes an increase in volume of the expansion material 801. Some examples of such material include chemically inert but thermally responsive plastics.

Fig. 8A shows valve 803 when the temperature is sufficiently low that the valve is open. That is, the volume of expansion material 801 is small enough that neat methanol or aqueous methanol solution can pass through a space between materials 801 and 802. When the temperature rises sufficiently, as illustrated in Fig. 8B, material 801 expands and closes the space, thus limiting the volume of fuel solution flowing through valve 803 to DMFC power system 200 or 300. By selecting materials 801 and 802 with appropriate thermal expansion coefficients, valve 803 may regulate the flow of

- 9 -

fuel, and thus functionally replace controller 501, temperature sensor 502 and valve 503.

Referring now to Figs. 5 and 9, a method of controlling DMFC temperature, which method is preferably implemented through appropriate programming of controller 501, is described. At step 901, controller 501 receives a signal indicative of the current temperature in the DMFC. As described above, temperature in the DMFC may be measure directly or indirectly in a variety of ways. At step 902, controller 501 determines whether the current temperature is within an optimal temperature range, above the range or below the range. If the temperature is within the optimal range or above the range, controller 501 does not release any methanol through valve 503. Instead, controller 501 waits at step 903 for a predetermined period of time before the DMFC's temperature is measured again.

If the current temperature in the DMFC is below the optimal range, controller 501, at step 904, references a counter or previously stored value to determine how much methanol has been previously released for increasing the temperature in the DMFC. The aggregate amount of methanol that can be released for this purpose is preferably limited such that methanol concentration within the DMFC remains within an optimal range. Thus, additional methanol will be released at step 905 provided that the aggregate limit has not been reached. It should be understood that additional control steps may be added to control the release of methanol.

It should be understood that at least some of the foregoing embodiments of the present invention may be used with direct oxidation fuel cells other than DMFCs.

What is claimed is:

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## **CLAIMS**

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- 1 1. A fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode
- 3 and cathode;
- a source of air or oxygen coupled to the cathode;
- a source of carbonaceous fuel; and
- a temperature regulation system, coupled to said source of fuel and said anode,
- 7 responsive to a temperature of said system such that when said temperature is below a
- 8 predetermined temperature or temperature range, said system increases fuel concentra-
- 9 tion at said anode to promote fuel cross-over through said membrane, thereby causing
- or increasing oxidation of some of said cross-over fuel at said cathode and increasing
- the temperature of said system.
- 1 2. The fuel cell system as in claim 1 wherein said temperature regulation system
- 2 comprises a temperature sensor for generating a signal indicative of the temperature of
- 3 said system.
- 1 3. The fuel cell system as in claim 2 wherein said temperature regulation system
- 2 further comprises a controller coupled to said sensor and responsive to said signal for
- determining whether additional fuel should be provided to said anode to increase the
- 4 temperature of said system.
- 1 4. The fuel cell system as in claim 3 wherein said temperature regulation system
- 2 further comprises a valve, coupled to and responsive to said controller, for varying the
- amount of fuel provided from said source to said anode.
- The fuel cell system as in claim 1 wherein temperature regulation system con-
- trols fuel concentration in response to an electrical parameter of said fuel cell system
- which has a predetermined relationship to the fuel cell system's temperature and a sig-
- anal, generated by a controller, that the fuel cell system's temperature is below said pre-
- 5 determined temperature or temperature range.

-11-

- 1 6. A fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode
- 3 and cathode;
- a source of air or oxygen coupled to the cathode;
- a source of carbonaceous fuel; and
- a temperature regulation system, coupled to said source of fuel and said cath-
- ode, responsive to a temperature of said system such that when said temperature is be-
- low a predetermined temperature or temperature range, said system applies fuel directly
- 9 into said cathode, thereby causing oxidation of fuel at said cathode and increasing the
- temperature of said system.
- 7. The fuel cell system as in claim 6 wherein said temperature regulation system
- 2 comprises a temperature sensor for generating a signal indicative of the temperature of
- 3 said system.

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- 1 8. The fuel cell system as in claim 7 wherein said temperature regulation system
- 2 further comprises a controller coupled to said sensor and responsive to said signal for
- determining whether additional fuel should be provided to said anode to increase the
- 4 temperature of said system.
- 1 9. The fuel cell system as in claim 8 wherein said temperature regulation system
- 2 further comprises a valve, coupled to and responsive to said controller, for varying the
- 3 amount of fuel provided from said source to said anode.
- 1 10. The fuel cell system as in claim 6 wherein temperature regulation system con-
- trols fuel concentration in response to an electrical parameter of said fuel cell system
- which has a predetermined relationship to the fuel cell system's temperature and a sig-
- anal, generated by a controller, that the fuel cell system's temperature is below said pre-
- 5 determined temperature or temperature range.
- 1 11. A fuel cell system, said system comprising:

-12-

PCT/US02/04161

- an anode, a cathode, and a membrane electrolyte disposed between the anode and cathode;
- a source of air or oxygen coupled to the cathode;
- a source of carbonaceous fuel; and
- a temperature regulation system for controlling the fuel cell system's tempera-
- ture by controlling delivery of fuel from said source to said anode or cathode, or by
- s controlling the flow of fuel through a conduit which generates heat by oxidation of at
- 9 least some of the fuel flowing through said conduit.
- 1 12. The fuel cell system as in claim 10 wherein said temperature regulation system
- 2 controls fuel delivery in response to a current or voltage produced by said fuel cell
- 3. system and a signal indicating that the fuel cell system's temperature is below a prede-
- 4 termined temperature range.
- 1 13. A fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode
- 3 and cathode;

WO 02/071520

- a source of air or oxygen coupled to the cathode;
- a source of carbonaceous fuel; and
- a conduit for generating heat to raise the fuel cell system's temperature, said
- 7 conduit coupled to said fuel source and having an interior sidewall which includes a
- 8 catalyst, said sidewall permitting admission of air into said conduit, whereby as fuel
- 9 flows through said conduit and across said catalyst, some of said fuel is oxidized.
- 1 14. The fuel cell system as in claim 13 wherein said conduit comprises a plurality of
- 2 conduit branches, associated valves and a controller, whereby heat generation is in-
- 3 creased by controlling the valves to allow fuel to flow through a larger number of
- branches and is decreased by restricting said flow to a smaller number of branches.
- 1 15. The fuel cell system as in claim 13 further comprising means for controlling the
- admission of air into said conduit, thereby controlling the amount of heat generated.

- 1 16. A fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode and cathode;
- a source of air or oxygen coupled to the cathode;
- a source of carbonaceous fuel; and
- one or more thermally actuated control valves, coupled to said fuel source, for
- 7 controlling the flow of fuel through a conduit, said valve constructed of two or more
- 8 different materials, the first material having a relatively low thermal expansion coeffi-
- 9 cient and the second material having a relatively high thermal expansion coefficient,
- whereby at relatively cold temperatures, said valve is open, and at relatively warm tem-
- peratures said valve is closed.

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- 1 17. A method of controlling temperature in a direct methanol fuel cell system, said method comprising the steps of:
- 3 (1) sensing a temperature in said system;
- 4 (2) determining whether the sensed temperature is below a predetermined tem-5 perature or temperature range;
- 6 (3) when said sensed temperature is not below the predetermined temperature 7 or range, repeating steps (1) and (2);
  - (4) when said sensed temperature is below the predetermined temperature or range, determining how much methanol fuel has previously been delivered to said system for the purpose of raising the temperature of said system;
  - (5) when the amount of fuel previously delivered to said system for the purpose of raising the temperature of the system is less than a predetermined maximum limit, releasing fuel in such a manner as to cause or increase oxidation of such fuel, thereby generating heat and raising the temperature of the system.
- 1 18. The method as in claim 17 wherein in step (5), fuel is released to an anode of
- said system to promote fuel cross-over through a membrane electrolyte, thereby caus-
- 3 ing or increasing oxidation of some of said cross-over fuel at a cathode and increasing
- 4 the temperature of said system.

-14-

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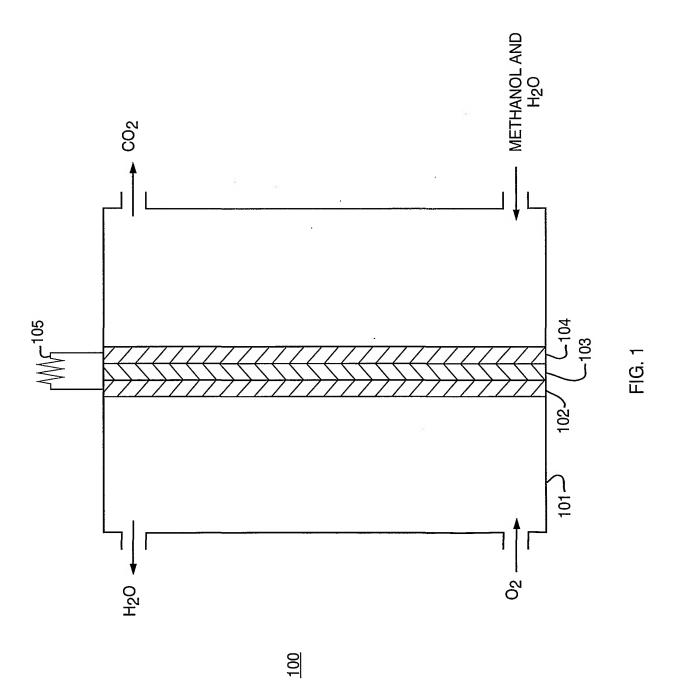
- 1 19. The method as in claim 17 wherein in step (5), fuel is released to a cathode of
- said system, thereby causing or increasing oxidation of fuel at said cathode and in-
- 3 creasing the temperature of said system.

WO 02/071520

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- 1 20. The method as in claim 17 wherein in step (5), fuel is released through a con-
- duit, said conduit having an interior sidewall which includes a catalyst, said sidewall
- 3 permitting admission of air into said conduit, whereby as fuel flows through said con-
- 4 duit and across said catalyst, some of said fuel is oxidized and generates heat.
- 1 21. The method as in claim 20 wherein said conduit comprises a plurality of conduit
- branches, associated valves and a controller, whereby heat generation is increased by
- 3 controlling the valves to allow fuel to flow through a larger number of branches and is
- decreased by restricting said flow to a smaller number of branches.
- 1 22. The method as in claim 20 wherein the admission of air into said conduit is
- 2 controlled, thereby controlling the amount of heat generated.
- 1 23. A method of controlling temperature in a direct methanol fuel cell system, said 2 method comprising the steps of:
- 3 (1) sensing an electrical parameter in said system, including either current or 4 voltage, which has a predetermined relationship to said fuel cell system's temperature;
- 5 (2) determining whether said fuel cell system's temperature is below a prede-6 termined temperature range;
  - (3) when said temperature is not below said predetermined range repeating steps (1) and (2);
- 9 (4) when said temperature is below said predetermined range increasing the 10 amount of fuel introduced to the system.



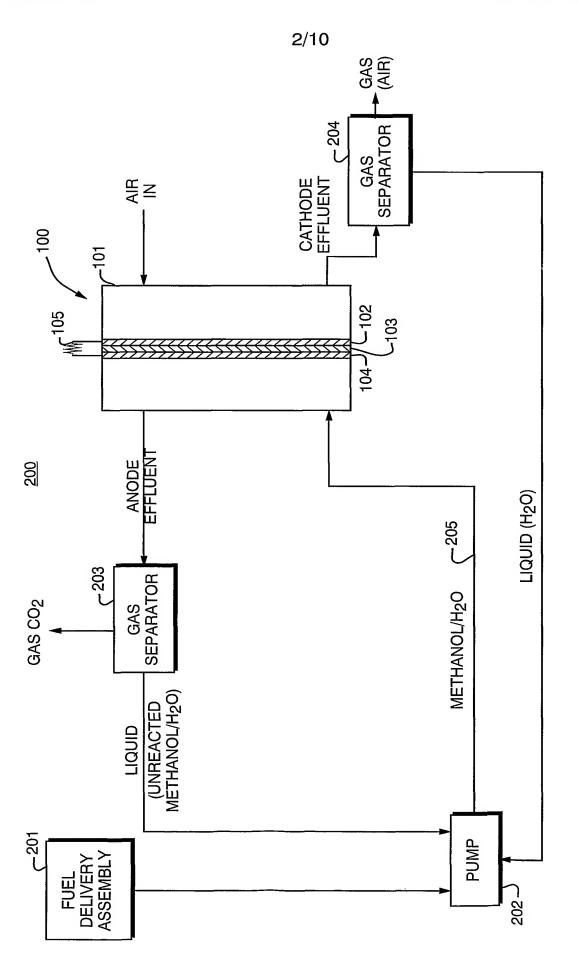
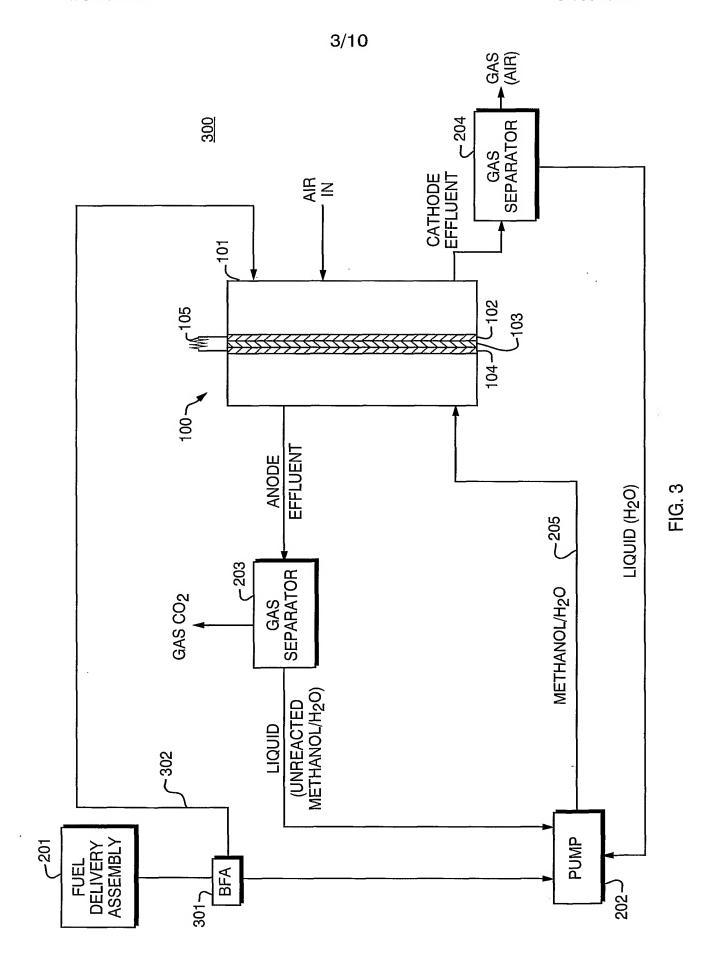
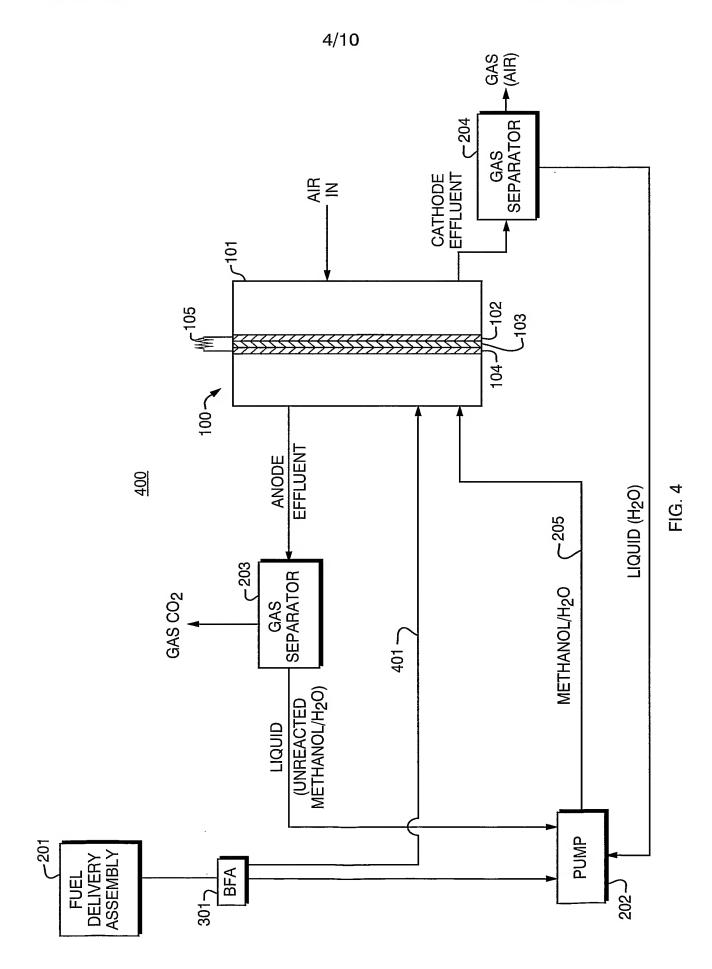


FIG. 2





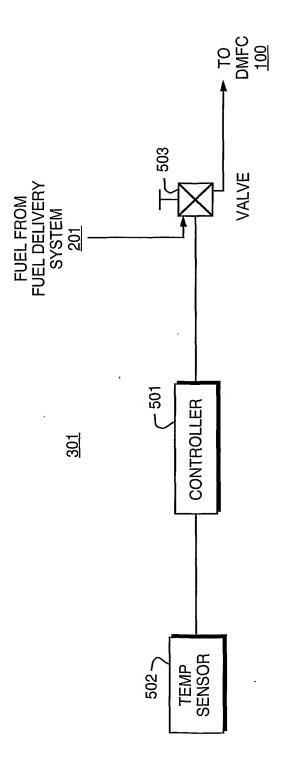


FIG. 5

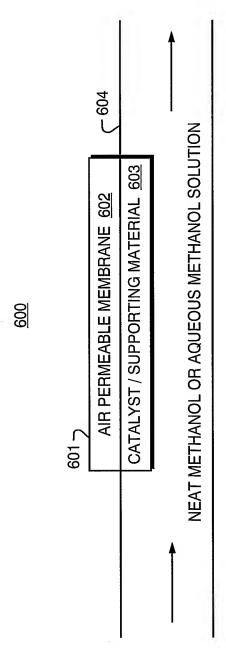
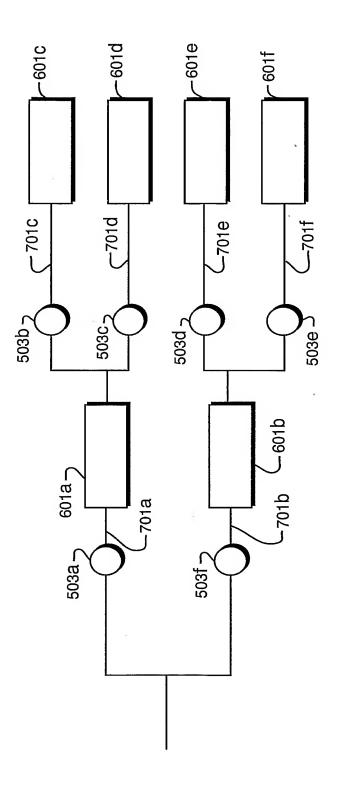
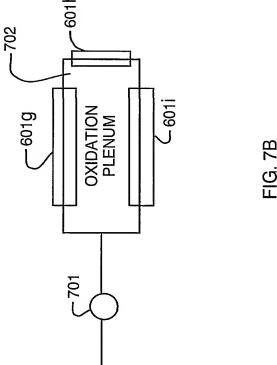


FIG. 6



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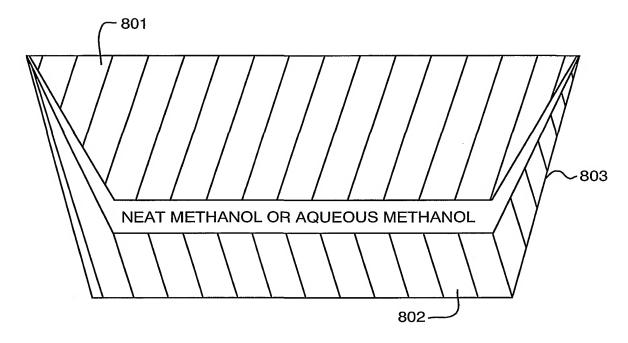


FIG.8A

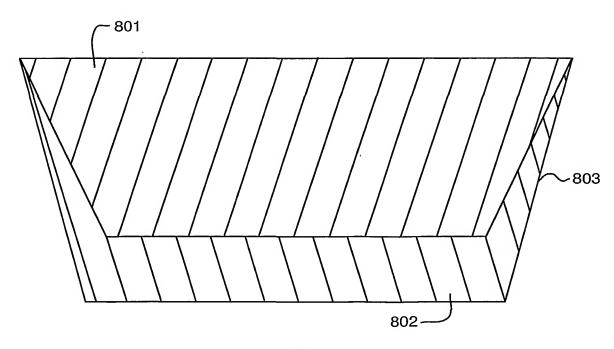


FIG.8B

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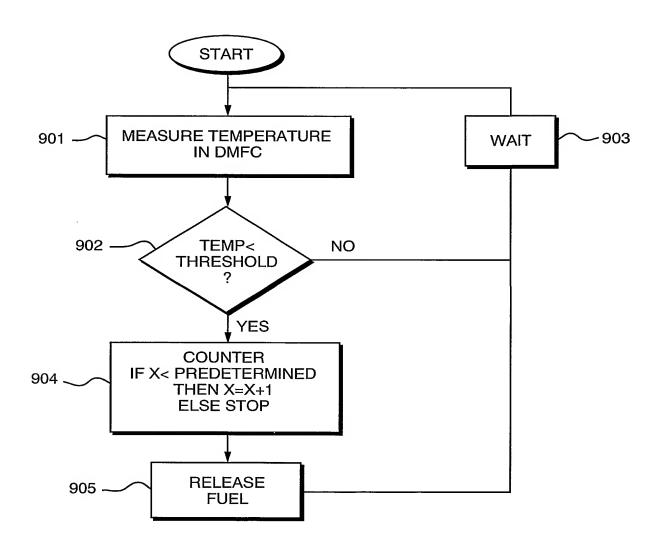


FIG. 9

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/04161

A. CLASSIFICATION OF SUBJECT MATTER  IPC(7) : H01M 8/00,8/7,8/12, 4/00  US CL : 429/13,22,24,26  According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) U.S.: H01M 8/00, 8/4, 8/12, 4/00				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched .				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where ap		Relevant to claim No.	
Х	US 4,046,956 A (FANCIULLO) 6 September 1977 (6.09.97), column 5 line 16 to column 6 line 48.		1-12 and 17-23	
Х	US 4,670,359 A (BESHTY et al) 2 June 1987 (2.06.1987), column 5 line 56 et seq.		13-15	
x	US 4,593,534 A (BLOOMFIELD) 10 June 1986 (10.	06.1986), column 5 line 7 et seq.	16	
	documents are listed in the continuation of Box C.	See patent family annex.		
Special categories of cited documents:  "A" document defining the general state of the art which is not considered to be of particular relevance		T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier application or patent published on or after the international filing date		"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		considered to involve an inventive ste combined with one or more other sucl	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means  "P" document published prior to the international filing date but later than the		"&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international sear	ch report	
31 May 2002 (31.05.2002)				
Name and mailing address of the ISA/US		Authorized officer	1	
Commissioner of Patents and Trademarks Box PCT		Julian A. Mercado Jean	Proctor Processing	
Washington, D.C. 20231 Facsimile No. (703)305-3230		Telephone No. (703) 308-0661	ToBar Shedrassa	

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/04161

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)			
This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:			
1. Claim Nos.: because they relate to subject matter not required to be searched by this Authority, namely:			
2. Claim Nos.:  because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:			
3. Claim Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).			
Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)			
This International Searching Authority found multiple inventions in this international application, as follows: Please See Continuation Sheet			
<ol> <li>As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.</li> <li>As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.</li> <li>As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:</li> </ol>			
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  Remark on Protest  The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.			

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/04161

#### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-12 and 17-23, drawn to a fuel cell system with a temperature regulation system.

Group II, claim(s) 11 and 13-23, drawn to a fuel cell system with a conduit,

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Groups I and II share the special technical feature of a fuel cell system having an anode, a cathode, and a source of carbonaceous fuel. As these special technical features do not define a contribution to the art as shown by U.S. Patent 4,046,956 to Fanciullo, unity of invention is therefore lacking.

Of note, claim 11 has been grouped in both Groups I and II as this claim recites (in the alternative) a temperature regulation system, or, a conduit for generating heat. Additionally, the method claims have been grouped in both Groups I and II as the method limitations appear to be functional recitations of either invention's structural limitations, and examination of the method claims along with either Group I or II required no additional effort on the part of the examiner.

## (19) World Intellectual Property Organization International Bureau





## (43) International Publication Date 12 September 2002 (12.09.2002)

#### **PCT**

# (10) International Publication Number WO 02/071520 A1

(51) International Patent Classification<sup>7</sup>: H01M 8/00, 8/12, 4/00

(21) International Application Number: PCT/US02/04161

(22) International Filing Date: 13 February 2002 (13.02.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

09/798,314 2 March 2001 (02.03.2001) US

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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

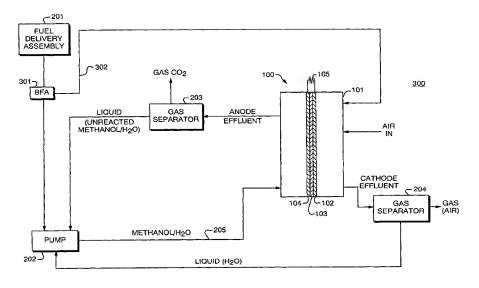
#### Published:

- with international search report
- with amended claims

Date of publication of the amended claims: 14 November 2002

[Continued on next page]

(54) Title: COLD START AND TEMPERATURE CONTROL METHOD AND APPARATUS FOR FUEL CELL SYSTEM



(57) Abstract: A fuel cell (100) which provides improved performance during a cold start. Several embodiments are provided to enable the controlled introduction of fuel into the cathode (202) of the fuel cell (100) such that oxidation occurs, heat is released and the temperature of the fuel cell (100) is raised. Such fuel may be introduced into the cathode (202) directly or may be introduced into the anode (204) and allowed to crossover an electrolytic membrane. Alternatively, the fuel may be directed through a special conduit (205) which allows oxidation of some of the fuel as it flows through.



## WO 02/071520 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

#### AMENDED CLAIMS

[received by the International Bureau on 23 August 2002 (23.08.02); original claims 1-16 amended; remaining claims unchanged (5 pages)]

- 1 1. A direct oxidation fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode and cathode;
- a source of air or oxygen coupled to the cathode;
- 5 a source of carbonaceous fuel; and
- a temperature regulation system, coupled to said source of fuel and said anode,
- 7 responsive to a temperature of said system such that when said temperature is below a
- 8 predetermined temperature or temperature range, said system increases fuel concentra-
- 9 tion at said anode to promote fuel cross-over through said membrane, thereby causing
- or increasing oxidation of some of said cross-over fuel at said cathode and increasing
- the temperature of said system.
- 1 2. The direct oxidation fuel cell system as in claim 1 wherein said temperature
- 2 regulation system comprises a temperature sensor for generating a signal indicative of
- 3 the temperature of said system.
- 1 3. The direct oxidation fuel coll system as in claim 2 wherein said temperature
- 2 regulation system further comprises a controller coupled to said sensor and responsive
- to said signal for determining whether additional fuel should be provided to said anode
- 4 to increase the temperature of said system.
- 1 4. The direct oxidation fuel cell system as in claim 3 wherein said temperature
- 2 regulation system further comprises a valve, coupled to and responsive to said control-
- 3 ler, for varying the amount of fuel provided from said source to said anode.
- 1 5. The direct oxidation fuel cell system as in claim 1 wherein said temperature
- 2 regulation system controls fuel concentration in response to an electrical parameter of
- said fuel cell system which has a predetermined relationship to the fuel cell system's
- 4 temperature and a signal, generated by a controller, that the fuel cell system's tem-
- 5 perature is below said predetermined temperature or temperature range,

- 1 6. A direct oxidation fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode
- 3 and cathode;
- a source of air or oxygen coupled to the cathode;
- s a source of carbonaceous fuel; and
- a temperature regulation system, coupled to said source of fuel and said cath-
- 7 ode, responsive to a temperature of said system such that when said temperature is be-
- low a predetermined temperature or temperature range, said system applies fuel directly
- 9 into said cathode, thereby causing oxidation of fuel at said cathode and increasing the
- temperature of said system.
- 1 7. The direct oxidation fuel cell system as in claim 6 wherein said temperature
- 2 regulation system comprises a temperature sensor for generating a signal indicative of
- 3 the temperature of said system.
- 1 8. The direct oxidation fuel cell system as in claim 7 wherein said temperature
- 2 regulation system further comprises a controller coupled to said sensor and responsive
- to said signal for determining whether additional fuel should be provided to said anode
- 4 to increase the temperature of said system.
- 1 9. The direct oxidation fuel cell system as in claim 8 wherein said temperature
- 2 regulation system further comprises a valve, coupled to and responsive to said control-
- 3 ler, for varying the amount of fuel provided from said source to said anode.
- 1 10. The direct oxidation fuel cell system as in claim 6 wherein temperature regula-
- 2 tion system controls fuel concentration in response to an electrical parameter of said
- fuel cell system which has a predetermined relationship to the fuel cell system's tem-
- 4 perature and a signal, generated by a controller, that the fuel cell system's temperature
- s is below said predetermined temperature or temperature range.
  - 11. A direct oxidation fuel cell system, said system comprising:

an anode, a cathode, and a membrane electrolyte disposed between the anode and cathode;

- a source of air or oxygen coupled to the cathode;
- s a source of carbonaceous fuel; and
- a temperature regulation system for controlling the fuel cell system's tempera-
- ture by controlling delivery of fuel from said source to said anode or cathode, or by
- s controlling the flow of fuel through a conduit which generates heat by oxidation of at
- 9 least some of the fuel flowing through said conduit.
- 1 12. The direct oxidation fuel cell system as in claim 10 wherein said temperature
- 2 regulation system controls fuel delivery in response to a current or voltage produced by
- said fuel cell system and a signal indicating that the fuel cell system's temperature is
- 4 below a predetermined temperature range.
- 1 13. A direct oxidation fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode and cathode;
- a source of air or oxygen coupled to the cathode;
- a source of carbonaceous fuel; and
- a conduit for generating heat to raise the fuel cell system's temperature, said
- 7 conduit coupled to said fuel source and having an interior sidewall which includes a
- s catalyst, said sidewall permitting admission of air into said conduit, whereby as fuel
- 9 flows through said conduit and across said catalyst, some of said fuel is oxidized.
- 1 14. The direct oxidation fuel cell system as in claim 13 wherein said conduit com-
- 2 prises a plurality of conduit branches, associated valves and a controller, whereby heat
- generation is increased by controlling the valves to allow fuel to flow through a larger
- 4 number of branches and is decreased by restricting said flow to a smaller number of
- 5 branches.

- 1 15. The direct oxidation fuel cell system as in claim 13 further comprising means
- 2 for controlling the admission of air into said conduit, thereby controlling the amount of
- 3 heat generated.
- 1 16. A direct oxidation fuel cell system, said system comprising:
- an anode, a cathode, and a membrane electrolyte disposed between the anode
- 3 and cathode;

11

12

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- a source of air or oxygen coupled to the cathode;
- a source of carbonaceous fuel; and
- one or more thermally actuated control valves, coupled to said fuel source, for
- 7 controlling the flow of fuel through a conduit, said valve constructed of two or more
- 8 different materials, the first material having a relatively low thermal expansion coeffi-
- 9 clent and the second material having a relatively high thermal expansion coefficient,
- whereby at relatively cold temperatures, said valve is open, and at relatively warm tem-
- 11 peratures said valve is closed.
- 1 17. A method of controlling temperature in a direct methanol fuel cell system, said
- 2 method comprising the steps of:
- 3 (1) sensing a temperature in said system;
- 4 (2) determining whether the sensed temperature is below a predetermined temperature or temperature range;
- 6 (3) when said sensed temperature is not below the predetermined temperature or range, repeating steps (1) and (2);
- (4) when said sensed temperature is below the predetermined temperature or range, determining how much methanol fuel has previously been delivered to said system for the purpose of raising the temperature of said system;
  - (5) when the amount of fuel previously delivered to said system for the purpose of raising the temperature of the system is less than a predetermined maximum limit, releasing fuel in such a manner as to cause or increase oxidation of such fuel, thereby generating heat and raising the temperature of the system.

- 1 18. The method as in claim 17 wherein in step (5), fuel is released to an anode of
- said system to promote fuel cross-over through a membrane electrolyte, thereby caus-
- 3 ing or increasing oxidation of some of said cross-over fuel at a cathode and increasing
- 4 the temperature of said system.
- 1 19. The method as in claim 17 wherein in step (5), fuel is released to a cathode of
- 2 said system, thereby causing or increasing oxidation of fuel at said cathode and in-
- 3 creasing the temperature of said system.
- 1 20. The method as in claim 17 wherein in step (5), fuel is released through a con-
- duit, said conduit having an interior sidewall which includes a catalyst, said sidewall
- 3 permitting admission of air into said conduit, whereby as fuel flows through said con-
- 4 duit and across said catalyst, some of said fuel is oxidized and generates heat.
- t 21. The method as in claim 20 wherein said conduit comprises a plurality of conduit
- branches, associated valves and a controller, whereby heat generation is increased by
- 3 controlling the valves to allow fuel to flow through a larger number of branches and is
- decreased by restricting said flow to a smaller number of branches.
- 1 22. The method as in claim 20 wherein the admission of air into said conduit is
- 2 controlled, thereby controlling the amount of heat generated.
- 1 23. A method of controlling temperature in a direct methanol fuel cell system, said
- 2 method comprising the steps of:
- 3 (1) sensing an electrical parameter in said system, including either current or
- 4 voltage, which has a predetermined rolationship to said fuel cell system's temperature;
  - (2) determining whether said fuel cell system's temperature is below a prede-
- 6 termined temperature range;
- 7 (3) when said temperature is not below said predetermined range repeating
- s steps (1) and (2);

5

- 9 (4) when said temperature is below said predetermined range increasing the
- amount of fuel introduced to the system.